# A SUMMARY OF MULTIPLE ORGANOPHOSPHATE DEGRADATION STUDIES ON LEAF FOLIAGE IN MONTEREY COUNTY IN 1984

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## SUMMARY

Multiple organophosphate applications (in one tank mix) are often made on row crops in the Salinas Valley of California. The materials used are a combination of contact and systemic insecticides. The resulting reentry intervals vary according to the combination of pesticides in each tank mix. Thirteen fields (5 cauliflower, 5 head lettuce, 2 Chinese cabbage, and 1 broccoli) were sampled for a number of different dislodgeable foliar pesticide residues after an application of two or more organophosphates. Leaf samples were collected before the applications, immediately after application and periodically for four to seven days post-application. In all but three cases, the residues were below the safe levels estimated by Knaak, et al. The three exceptions being mevinphos on Chinese cabbage (2 fields) and oxydemeton-methyl on cauliflower. Further study is needed to determine the reasons for the high residues found in these fields.

## INTRODUCTION

From 1949 through the present, records have been kept on multiple case field worker poisoning incidents in California involving exposure to organophosphate (OP) insecticides (1). Through 1983, at least 38 such incidents have been noted; at least 65% of these have involved parathion. The severity of the resulting illnesses is presumed to be dependent on the amount and toxicity of residue on the leaf surface, the extent and duration of contact with the foliage (2), and possibly, contact with contaminated soil particles in the treated area (3).

As a result of the increasing number of these incidents, the California Department of Food and Agriculture (CDFA) established reentry intervals to protect field workers from exposure to high residues on crops (4). Many of the reentry intervals in effect today were set in 1971 (with very limited information) on the basis of reported illnesses, crops involved and the time lapse from application to the onset of illness.

Since that time, dermal dose-response studies in laboratory animals (5,6) and controlled human testing (7) have been used to calculate residue levels on foliage which will not cause illness upon prolonged contact. These "safe levels", along with foliar degradation data, can be used to determine a reentry interval. There are however, some factors that may affect the degradation profile, these include: 1) application and dilution rate, 2) application method and equipment, 3) temperature, 4) humidity, 5) irrigation practices, and 6) airborne oxidants. These variables suggest the need for either variable reentry intervals (based on temperature, application rate, etc.) or the addition of a safety factor to the "safe levels".

Reentry intervals required in California are established for individual chemicals (See Appendix I). However, some pest management practices in vegetable crops often call for an application of two or more OP's in one tank mix. Intervals for mixtures of organophosphates, as used in Monterey County, are determined by adding to the longest interval 50 percent of the next longest interval (8). Since many of the more toxic Category I OP's in use have 48-hour reentry intervals on vegetable crops, 72-hour reentry intervals are common. These studies were conducted to determine the adequacy of present reentry regulations in mitigating health hazards to workers entering fields previously treated with two or more OP's.

## METHODS AND MATERIALS

With the assistance of the staffs of the Monterey and Santa Cruz County Agricultural Commissioners, pending applications were determined from Notices of Intent to apply Restricted Materials. Cooperation was obtained from growers, pest control advisors, and operators who would be applying two or more organophosphate pesticides in one tank mix. The materials used included various combinations of dimethoate (Cygon), oxydemeton-methyl (Metasystox-R), mevinphos (Phosdrin), phosphamidon (Dimecron), or Diazinon. The reentry intervals varied according to the combination of pesticides applied. See Appendix 1 for the application rates and other pertinent information for each application.

Foliar samples were drawn using the methods described by Gunther, et. al., (9) and Iwata, et al. (2). Each selected field was divided into three areas. Non-adjacent rows from each of these areas were chosen as the rows to be sampled. One sample consisted of a composite of 16 leaf punches collected from each of the rows; eight on the right of the row and eight on the left of each row. Punches were taken from leaves presenting the greatest exposed surface area. Three replicate samples were obtained at each sampling interval from sites spaced to collect a sample representative of the entire field.

Pre-application samples were collected before each application. Post-application samples were taken immediately following the application and periodically throughout a period of four to seven days.

Leaf punches were collected using a 2.54 cm diameter leaf punch. Each sample contained 48 leaf discs accumulated in a four ounce glass jar. The leaf punch was cleaned with alcohol between sampling rows. Sample jars were sealed with aluminum foil, capped, and stored on wet ice. (All required protective equipment was worn by personnel collecting the samples.)

Samples were analyzed in the Worker Safety mobile chemistry laboratory which was on-site in Monterey County for the duration of this study. Foliar residues were extracted from the leaf in a water/surfactant solution. The aqueous solution was then solvent extracted. The solvent extract was reduced in volume and a known amount of ethyl acetate was added. The extracts were then analyzed by gas chromatography. For oxydemeton- methyl, the residues in the ethyl acetate were oxidized to the sulfone and extracted with methylene chloride. This extract was reduced in volume and replaced with iso-octane. The extract was then analyzed by gas chromatography.

## RESULTS

The results of our findings are presented in the following tables and graphs.

Field 1 and Field 13 (Chinese cabbage) were treated with mevinphos and Diazinon by ground rig. The results are shown in Table 1 and Figure 1. The residues in Field 1 were consistently higher than those in Field 13. The mevinphos residue in both fields was above the safe level at the expiration of the fields reentry intervals.

Fields 2 through 6 (head lettuce) were all treated with Diazinon and mevinphos by ground rig. Table 2 displays the results from those applications.

TABLE 1

Mevinphos and Diazinon Residue on Chinese Cabbage

| Sample Interval | FIELD 1 Mean Residue ($ug/cm^2$) Mevinphos | FIELD 1 Mean Residue ($ug/cm^2$) Diazinon | Sample Interval | FIELD 13 Mean Residue ($ug/cm^2$) Mevinphos | FIELD 13 Mean Residue ($ug/cm^2$) Diazinon |
|---|---|---|---|---|---|
| PRE-APP | 0.1 | - | PRE-APP | - | - |
| 0.5 Hours | 0.966 | 0.221 | 8 Hours | 0.283 | 0.083 |
| 8 Hours | 0.338 | 0.170 | 16 Hours | 0.280 | 0.041 |
| 12 Hours | 0.440 | 0.073 | 32 Hours | 0.132 | 0.025 |
| 24 Hours | 0.189 | 0.047 | 40 Hours | 0.087 | 0.018 |
| 36 Hours | 0.331 | 0.050 | 56 Hours | 0.102 | 0.013 |
| 48 Hours | 0.104 | 0.015 | 63 Hours | 0.045 | 0.005 |
| | | | 80 Hours | 0.033 | 0.004 |

* Average Temperature:
Maximum - 64.5°F
Minimum - 42.3°F

* Average Temperature:
Maximum - 73.8°F
Minimum - 56.4°F

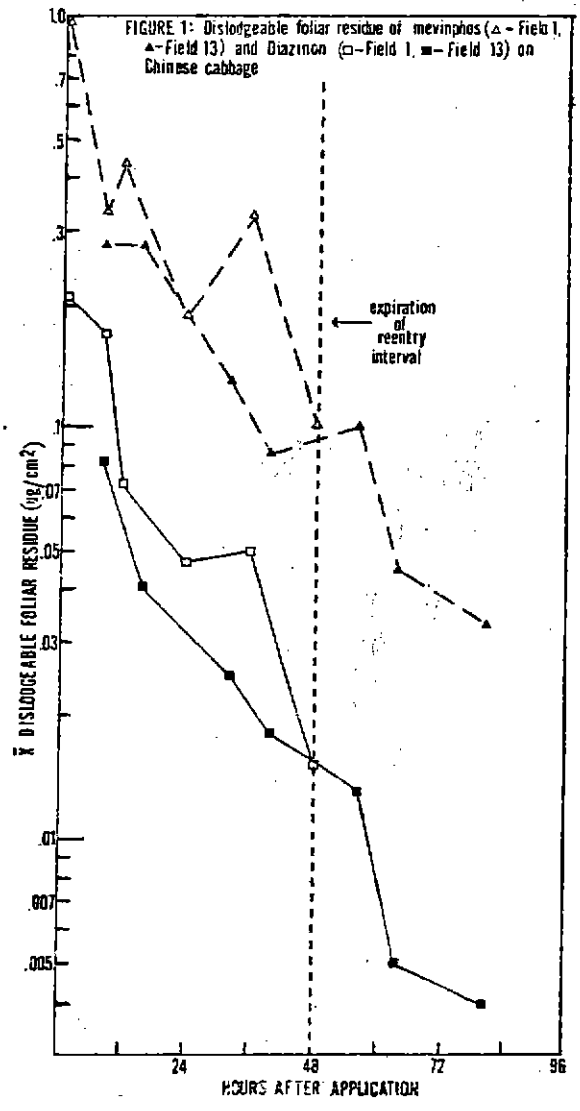
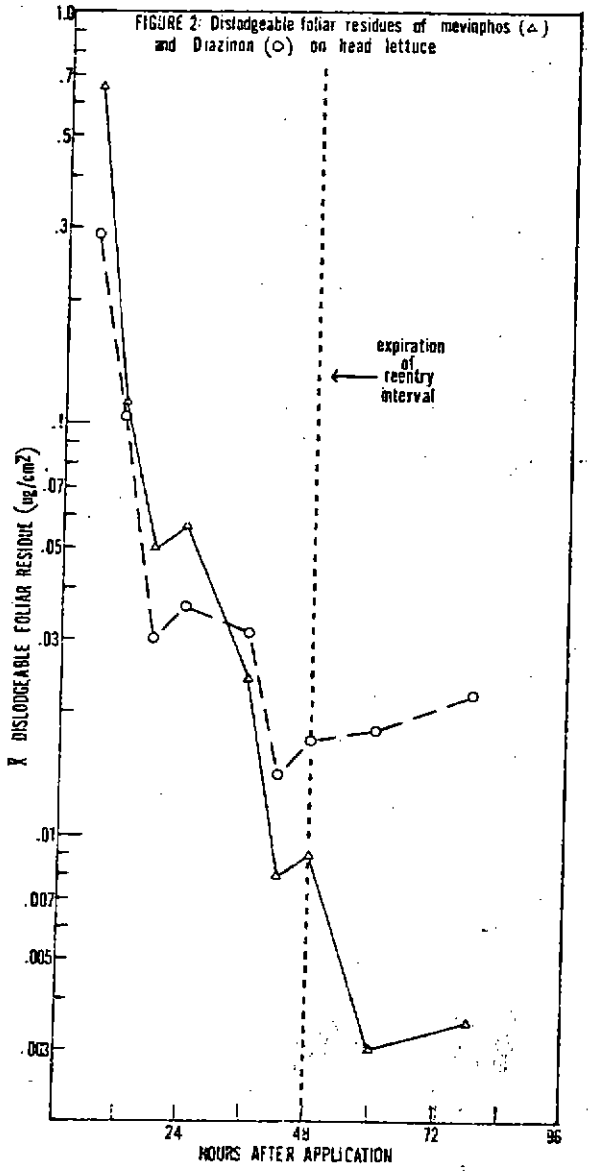


TABLE 2

Foliar Mevinphos and Diazinon Residues (ug/cm$^2$) Following Application to Head Lettuce

| | CHEMICAL | SAMPLE INTERVAL | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Pre-Application | 6 Hours | 12 Hours | 18 Hours | 24 Hours | 36 Hours | 42 Hours | 48 Hours | 60 Hours | 78 Hours |
| Field 2 | Mevinphos | 0.0002 | 0.214 | 0.130 | NS | 0.029 | 0.020 | NS | 0.025 | NS | NS |
| | Diazinon | ND | 0.186 | 0.129 | NS | 0.030 | 0.030 | NS | 0.020 | NS | NS |
| Field 3 | Mevinphos | ND | 0.885 | 0.185 | 0.089 | 0.115 | 0.030 | 0.010 | 0.008 | 0.003 | 0.004 |
| | Diazinon | 0.0002 | 0.367 | 0.180 | 0.054 | 0.054 | 0.049 | 0.033 | 0.031 | 0.016 | 0.019 |
| Field 4 | Mevinphos | ND | 0.877 | 0.154 | 0.067 | 0.118 | 0.046 | 0.014 | 0.009 | 0.004 | 0.003 |
| | Diazinon | 0.0002 | 0.346 | 0.124 | 0.032 | 0.078 | 0.059 | 0.008 | 0.021 | 0.046 | 0.025 |
| Field 5 | Mevinphos | ND | NS | 0.079 | 0.029 | 0.014 | 0.010 | 0.007 | 0.003 | 0.003 | NS |
| | Diazinon | ND | NS | 0.056 | 0.017 | 0.010 | 0.006 | 0.007 | 0.006 | 0.004 | NS |
| Field 6 | Mevinphos | ND | NS | 0.015 | 0.008 | 0.003 | 0.013 | 0.001 | 0.001 | 0.001 | NS |
| | Diazinon | ND | NS | 0.032 | 0.017 | 0.008 | 0.011 | 0.006 | 0.008 | 0.006 | NS |
| Average | Mevinphos | < 0.001 | 0.658 | 0.112 | 0.049 | 0.056 | 0.024 | 0.008 | 0.009 | 0.003 | 0.003* |
| | Diazinon | < 0.001 | 0.288 | 0.104 | 0.030 | 0.036 | 0.031 | 0.014 | 0.017 | 0.018 | 0.022* |

* - Average was calculated from only two fields.
ND - None Detected
NS - No Sample Collected
Mimimum Detectable Level (MDL) - Mevinphos - 0.001
Diazinon - 0.002




As can be seen from Table 2 and Figure 2 the residues of both mevinphos and Diazinon dissipated quite rapidly. Both chemicals were below their respective estimated safe level (11) values (0.09 and 1.5 ug/cm$^2$) prior to the expiration of the 48-hour reentry interval. (Diazinon by the 12-hour post-application sample and mevinphos by the 18-hour post-application sample.)

TABLE 3

Foliar Mevinphos, Oxydemeton-Methyl (MSR) and Phosphamidon Residues ($ug/cm^2$) Following Application to Cauliflower

| | CHEMICAL | SAMPLE INTERVAL | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Pre-Application | 6 Hours | 12 Hours | 16 Hours | 30 Hours | 36 Hours | 40 Hours | 54 Hours | 60 Hours | 78 Hours | 7 Days |
| Field 8 | MSR | ND | 0.115 | 0.094 | 0.042 | 0.096 | 0.102 | 0.091 | 0.093 | 0.127 | 0.068 | 0.032 |
| | Mevinphos | 0.001 | 0.041 | 0.033 | 0.032 | 0.028 | 0.039 | 0.016 | 0.031 | 0.027 | 0.009 | 0.0003 |
| | Phosphamidon | ND | 0.220 | 0.112 | 0.094 | 0.150 | 0.148 | 0.062 | 0.079 | 0.097 | 0.030 | 0.005 |
| Field 11 | MSR | ND | 0.079 | 0.070 | NS | 0.038 | 0.024 | NS | 0.025 | 0.032 | 0.026 | NS |
| | Mevinphos | ND | 0.069 | 0.032 | NS | 0.014 | 0.016 | NS | 0.008 | 0.007 | 0.003 | NS |
| | Phosphamidon | ND | 0.111 | 0.065 | NS | 0.036 | 0.034 | NS | 0.010 | 0.012 | 0.004 | NS |
| Field 12 | MSR | ND | 0.083 | 0.067 | NS | 0.049 | 0.045 | NS | 0.035 | 0.028 | 0.022 | NS |
| | Mevinphos | ND | 0.090 | 0.035 | NS | 0.026 | 0.020 | NS | 0.014 | 0.006 | 0.002 | NS |
| | Phosphamidon | ND | 0.089 | 0.049 | NS | 0.048 | 0.023 | NS | 0.009 | 0.007 | 0.003 | NS |
| Average | MSR | ND | 0.092 | 0.077 | 0.042* | 0.061 | 0.057 | 0.091* | 0.051 | 0.062 | 0.039 | 0.032* |
| | Mevinphos | 0.0001 | 0.067 | 0.033 | 0.032* | 0.023 | 0.025 | 0.016* | 0.018 | 0.013 | 0.005 | 0.0003* |
| | Phosphamidon | ND | 0.140 | 0.075 | 0.094* | 0.078 | 0.068 | 0.062* | 0.033 | 0.039 | 0.012 | 0.005* |

* Averages are from Field 8 only and are not included in Figure 3

ND - None Detected

NS - No Sample

MDL - MSR - 0.001

Mevinphos - 0.001

Phosphamidon - 0.001

Fields 8, 11 and 12 were treated with mevinphos, oxydemeton-methyl and phosphamidon. All three fields were treated by ground-rigs with boom-mounted sprayers. The results of sampling in these fields are displayed in Table 3 and Figure 3. The mean foliar residues of all three chemicals were below the respective interim safe levels (mevinphos - 0.09 ug/cm$^2$, oxydemeton-methyl 0.9 ug/cm$^2$ and phosphamidon 0.1 ug/cm$^2$) at the time of legal reentry (72 hours for this combination).

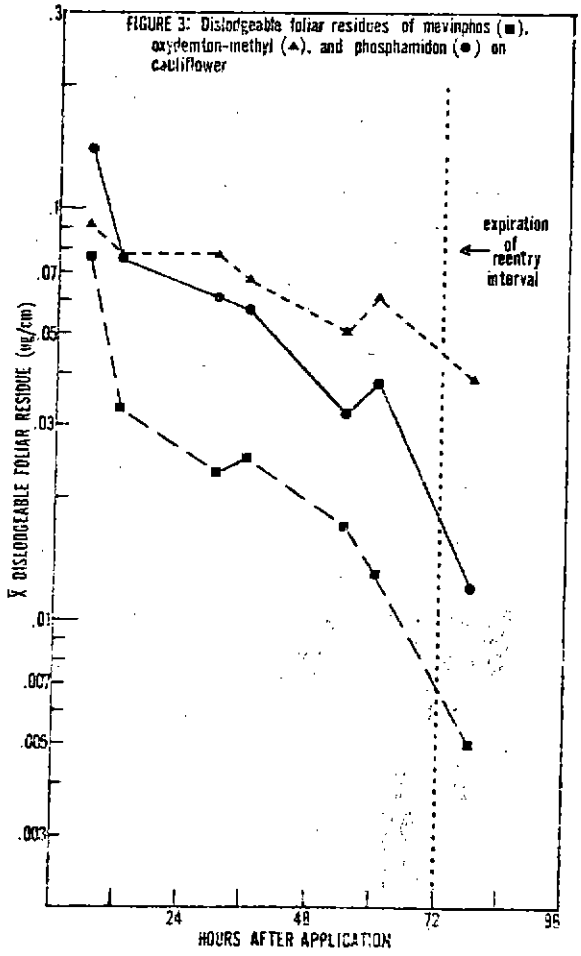
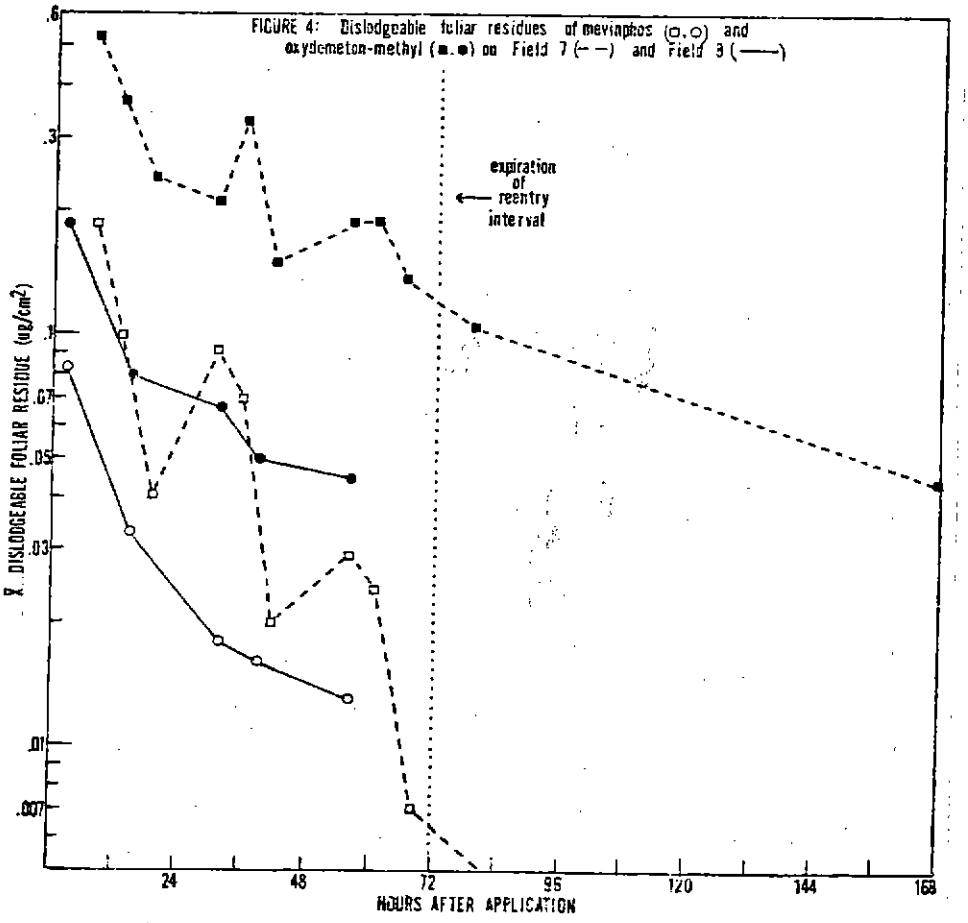


TABLE 4

Mean Foliar Oxydemeton-methyl (MSR) and Mevinphos Residues Following Application to Cauliflower (ug/cm$^2$).

| | FIELD 7 | | FIELD 9 | | |
|---|---|---|---|---|---|
| | MSR | Mevinphos | | MSR | Mevinphos |
| Pre-App. | ND | ND | Pre-App. | | 0.0007 |
| 8 Hours | 0.531 | 0.188 | 3 Hours | 0.186 | 0.083 |
| 13 Hours | 0.369 | 0.099 | 15 Hours | 0.080 | 0.033 |
| 19 Hours | 0.242 | 0.041 | 32 Hours | 0.067 | 0.018 |
| 31 Hours | 0.211 | 0.092 | 39 Hours | 0.050 | 0.016 |
| 36 Hours | 0.331 | 0.070 | 57 Hours | 0.045 | 0.013 |
| 42 Hours | 0.151 | 0.020 | | | |
| 56 Hours | 0.190 | 0.029 | | | |
| 61 Hours | 0.192 | 0.024 | | | |
| 66 Hours | 0.136 | 0.007 | | | |
| 79 Hours | 0.104 | 0.007 | | | |
| 7 Days | 0.044 | 0.0006 | | | |



As can be seen (Table 4 and Figure 4) for Field 7 the oxydemeton-methyl degraded a little slower than other fields. However, the dislodgeable residues were well below the safe level by the expiration of the reentry interval for this field. The other decay curves were also well below the estimated safe levels at 72 hours (the legal reentry for this combination of chemicals).

## DISCUSSION

From 1980 through 1983, two incidents in Monterey County were reported in which five or more people were exposed to two or more organophosphates in a tank mix via early field reentry. These incidents included applications of mevinphos and phosphamidon (reentry occurred 3 hours after application) and oxydemeton-methyl and dimethoate (reentry occurred 1 day early). A total of 37 workers became ill with symptoms typical of organophosphate poisoning.

These studies were conducted to determine the adequacy of present reentry regulations in mitigating health hazards to workers entering fields treated in this manner. Although past incidents indicate a great number of harvest worker illnesses are caused by organophosphate poisoning, many are the result of early reentry into treated areas.

With the exception of the mevinphos in Field 1 and 13, all residues were well below the estimated "safe levels" before the appropriate reentry interval had expired. Thus, according to available data, the current reentry intervals should be adequate to protect field workers in the other fields. Further study is needed for mevinphos on Chinese cabbage.

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APPENDIX I

Characterisitics of Applications Involving Two or More Organophosphates (OP's)

| Field # | Date of Application (1984) | Crop | OP's Used | Application Rate (lbs. A.I./Acre) | Dilution Rate (Gal./Acre) | Reentry Interval (Hours) | Other Chemicals in Tank Mix |
|---|---|---|---|---|---|---|---|
| 1 | 4 - 24 | Chinese Cabbage | Mevinphos<br>Diazinon | 0.25<br>0.35 | 60 | 48 | Methomyl, Maneb |
| 2 | 4 - 24 | Head Lettuce | Mevinphos<br>Diazinon | 0.50<br>0.50 | 100 | 48 | Permethrin, Mancozeb, Buffering Agent |
| 3 & 4 | 5 - 14 | Head Lettuce | Mevinphos<br>Diazinon | 0.50<br>0.50 | 100 | 48 | Permethrin, Mancozeb, Spreader-Sticker |
| 5 & 6 | 5 - 22 | Head Lettuce | Mevinphos<br>Diazinon | 0.50<br>0.50 | 100 | 48 | Permethrin, Mancozeb, Buffering Agent |
| 7 | 7 - 23 | Cauliflower | Mevinphos<br>Oxydemeton-methyl | 1.00<br>0.50 | 60 | 72 | Fenvalerate, Nutrient Concentrate |
| 8 | 7 - 23 | Cauliflower | Mevinphos<br>Oxydemeton-methyl<br>Phosphamidon | 1.00<br>0.50<br>1.00 | 75 | 72 | Penetrant-Spreader |
| 9 | 7 - 31 | Cauliflower | Mevinphos<br>Oxydemeton-methyl | 1.00<br>0.50 | 80 | 72 | Penetrant-Spreader |
| 10 | 7 - 31 | Broccoli | Oxydemeton-methyl<br>Dimethoate | 0.50<br>0.50 | 60 | 48 | Fenvalerate, Penetrant-Spreader |
| 11 & 12 | 8 - 13 | Cauliflower | Mevinphos<br>Oxydemeton-methyl<br>Phosphamidon | 1.00<br>0.50<br>0.75 | 60 | 72 | Fenvalerate, Penetrant-Spreader |
| 13 | 8 - 13 | Chinese Cabbage | Mevinphos<br>Diazinon | 0.25<br>0.50 | 60 | 72 | Endosulfan |